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Comment on "Nanometer resolution piezoresponse force microscopy to study deep submicron ferroelectric and ferroelastic domains" [Appl. Phys. Lett. 94, 162903 (2009)]

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In a recent article in this journal, Ivry *et al.*[1] report on the potential of piezoforce microscopy to investigate ferroelectric domain structures with very high spatial resolution. In the same paper, they describe the observation of nanometer-sized ferroelastic (a/c) domains in polycrystalline thin film ferroelectric samples. These domains within grains show a short-range periodicity that can be as small as 10 nm. This has led the authors to state that our claim of a minimum period length of 27 nm (Ref. 2) is incorrect. In our article, we have pointed out that the prediction of a *minimum a-domain size* of 6–7 nm (which gives rise to a *minimum a/c periodicity* of 27 nm for $PbTiO_3$ on $DyScO_3$) is valid for epitaxially grown thin films in which there is coherence across the domain walls. The key ingredient of our model is this cube-on-cube lattice coherence across the domain walls, as observed in the transmission electron microscopy images,[2] while coherence can be disrupted at the substrate interface by formation of disclinations, corrugation, etc. The reason for this behavior is not completely understood but we believe that the choice of substrate, its stiffness and chemical compatibility with the film are important factors determining the existence of coherence across the domain walls rather than coherence across the substrate interface.[3]

According to the proposed microscopic model,[2] when the domains form upon cooling through T_C, each a-domain exactly matches with the c-domain on its right-hand side and with the c-domain at its left-hand side. This is common for 90° twinning in $PbTiO_3$ and the characteristic twin angle α (Fig. 1) is given by the following c/a ratio:

$$\alpha = 90\,^\circ - 2\,\tan^{-1}(a/c). \tag{1}$$

Cooling an epitaxial thin film of $PbTiO_3$ on a substrate down from the cubic phase, poses the boundary condition that the total number of unit cells in one period should be equal for the thin film and its substrate:

$$N_c \times a + N_a \times c = N \times b, \tag{2}$$

with the number of unit cells in one period, one a-domain and one c-domain being N, N_a, and N_c, respectively, and a and c the tetragonal lattice parameters of the ferroelectric, b the cubic lattice parameter of the substrate. The lowest energy barrier to transform from a single-domain epitaxial thin film to this situation occurs when two adjacent c-domains are shifted with respect to each other just one lattice spacing in the vertical direction, so that the Bragg-planes on the adjacent c-domains are coplanar (Fig. 1). This can be written as

$$N_a^{\min} \times c = w_a^{\min} = c/\sin(\alpha). \tag{3}$$

Taking Eq. (1) into account, this leads to the smallest possible length of a-domains, fully determined by the c/a ratio, giving a value of 6–7 nm for $PbTiO_3$. This "geometric" microscopic model is in agreement with the observation of long-range ordered domains in films grown under conditions of lattice mismatch[2] in which the coherence is not disturbed by the presence of dislocations or other defects.

Whereas our observations were based on 30 nm $PbTiO_3$ films epitaxially grown on $DyScO_3$ $(110)_o$, the subject of Ivry's study are 190 nm thick polycrystalline $PbZr_{0.7}Ti_{0.3}O_3$ (PZT) samples deposited onto iridium. In general, our model will not apply to these samples in which domain formation is complicated by the presence of grain boundaries or other defects. Moreover, the random orientation of the grains means that the geometrical constraints at the heart of our model cannot easily be invoked, as the coplanarity between Bragg planes is thought to be linked to the epitaxial growth. By the same token, their measurements neither prove nor

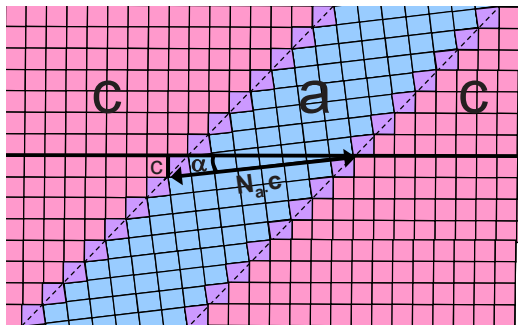

FIG. 1. (Color online) Schematic representation of our model showing the c/a/c-domain structure on a microscopic level. The larger c-domains on either side of the a-domain have atomic planes that are collinear (laterally coherent), and the combination of this colinearity with the tilting angle of the a-domains imposes a constraint on the minimum size of the a-domains: they must be such that there is exactly one unit cell height difference between the two sides. The lateral coherence is in turn thought to arise from the vertical coherence of the (larger) c-domains with the substrate. Since vertical coherence is due to epitaxy, epitaxy is a necessary condition of our model. It is also worth mentioning that, very close to the interface, the a-domains are themselves less tilted and less distorted, but a discussion of the exact distortions at the interface is beyond the scope of this comment.

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disprove our model. Ivry's reference to our article shows there is a need to clarify this point, and this is the aim of the present Comment. To reiterate, then, our minimum domain size is not an absolute minimum for all types of samples, it is the minimum equilibrium domain size that a/c ferroelastic domains can have in an epitaxially grown sample that keeps the lateral coherence upon domain formation. *Smaller domain sizes are possible* in either nonequilibrium configurations or in nonepitaxial samples and, therefore, it is unlikely that the same periodicity is found everywhere in the sample. The paper of Ivry is an example of this, since different periodicities, ranging from 10 to 50 nm or larger, can be observed in the different images (see also supplementary information of Ref. 1).

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